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<p>(21) International Application Number: PCT/US96/03081</p> <p>(22) International Filing Date: 5 March 1996 (05.03.96)</p> <p>(30) Priority Data: 472,152 7 June 1995 (07.06.95) US</p> <p>(71)(72) Applicant and Inventor: PASSLEY, Paul, Leonard [US/US]; Monsanto Company, 800 North Lindbergh Boulevard, St. Louis, MO 63167 (US).</p> <p>(72) Inventors: DAY, Thomas, McCabe; 439 Magna Carta Drive, Creve Coeur, MO 63141 (US). GILLESPIE, Jane, Laura; 7229 Cornell, University City, MO 63130 (US). KRAMER, Richard, Melvyn; 15238 Kingsman Circle, Chesterfield, MO 63017 (US). LINDEMANN, Ralph, Elmer, Jr.; 12943 Whitehorse Lane, St. Louis, MO 63131 (US).</p> <p>(74) Agent: PASSLEY, Paul, Leonard; Monsanto Company, 800 North Lindbergh Boulevard, St. Louis, MO 63167 (US).</p>		<p>(81) Designated States: AM, AU, AZ, BB, BG, BR, BY, CA, CN, CZ, EE, GE, HU, IS, JP, KG, KR, KZ, LK, LR, LT, LV, MD, MG, MK, MN, MX, NO, NZ, PL, RO, RU, SG, SI, SK, TJ, TM, TR, TT, UA, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</p> <p>Published <i>With international search report.</i></p>	
<p>(54) Title: PREPARATION OF AMMONIUM GLYPHOSATE USING AQUEOUS AMMONIUM HYDROXIDE IN A LIQUID-SOLID REACTION SYSTEM</p> <p>(57) Abstract</p> <p>Solid N-phosphonomethylglycine or glyphosate acid is charged to a substantially closed system and then partially pre-dried as by continuously recirculating it through a hot air grinding/drying system. A cooled solution of ammonium hydroxide is then metered into and reacted with the partially dried glyphosate acid as it is being recirculated in a manner such that the moisture content of the reaction mass so formed is continuously decreased throughout the reaction. Following completion of the ammonium hydroxide addition, a powdered reaction mass/product having a moisture content of about 2 wt.% is formed. Significantly, at this stage, the ammonium glyphosate product is suitable for end use and it can be readily dissolved in water and immediately used as a herbicide or plant growth regulator. More importantly, however, this product is capable due to its highly sorptive character to be further formulated into a product exceptionally highly loaded with adjuvants and particularly surfactants.</p>			

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**PREPARATION OF AMMONIUM GLYPHOSATE USING AQUEOUS
AMMONIUM HYDROXIDE IN A LIQUID-SOLID REACTION SYSTEM**

BACKGROUND

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Field of the Invention

This invention relates to a dry, non-clumping herbicidal composition together with a method for making the composition. More particularly, the present 10 invention relates to an ammonium glyphosate herbicide and an efficient method for making solid ammonium glyphosate products that readily dissolve in water and that can be used to prepare highly-loaded, adjuvant-containing dry/solid glyphosate compositions.

15

Description of the Related Art

N-phosphonomethylglycine [$\text{HOOCCH}_2\text{NH CH}_2\text{PO(OH)}_2$], which is commonly referred to as glyphosate acid or simply glyphosate, is well known in the art as a highly 20 effective herbicide. It is also known that glyphosate, an organic acid, has relatively low solubility in water. Thus, glyphosate is typically formulated as a water-soluble salt, particularly as the mono-isopropylamine (IPA) salt to kill or control weeds or plants.

25 Glyphosate is sold commercially as an aqueous concentrate in the form of its IPA salt by Monsanto Company of St. Louis, Missouri (U.S.A.) under the registered trademark Roundup®.

Various salts of glyphosate, methods for preparing 30 salts of glyphosate, formulations of glyphosate and methods of use for killing and controlling weeds and plants are disclosed in U.S. Patent Nos. 3,799,758 and 4,405,531 issued to John E. Franz on March 26, 1974 and September 20, 1983 respectively. Other U.S. Patents 35 which disclose salts of glyphosate include U.S. 4,315,765 issued to George B. Large on February 16,

1982, U.S. 4,507,250 issued to Izak Bakel on March 26,
1985, U.S. 4,397,676 issued to Izak Bakel on August 9,
1983, U.S. 4,481,026 issued to Michael P. Prisbylla on
November 6, 1984 and U.S. 4,140,513 issued to Erhard J.
5 Prill on February 20, 1979. All of the foregoing
patents, in their entireties, are herein incorporated by
reference.

Roundup® brand herbicide is sold as a water-soluble liquid concentrate. However, efforts have recently been
10 made in the art to develop a water-soluble dry/solid glyphosate formulation which has the equivalent efficacy of Roundup®. Conventional reasons underlying these efforts have been desired cost savings in connection with the packaging, shipment and storage of a solid
15 formulation versus a liquid. As can be appreciated, aqueous concentrates include a significant amount of solvent that adds to the size and weight of packaging containers and increases costs associated with post-manufacture delivery of the product to market.
20 A less readily apparent benefit also resides in the advantage of making a water-soluble, dry glyphosate. Namely, a granular formulation is believed to provide superior handling characteristics (i.e. controlled spillage) and is expected to be substantially lighter
25 and less awkward to transport (and often hand carry) thereby making the product better suited for use in remote geographic locations.
30 Making a solid granular glyphosate formulation, however, entails overcoming inherent disadvantages relating principally to the increased production cost and comparative complexity of compounding a solid product from a combination of liquid and solid reactants rather than making a product in solution from the same reactants.

Several methods for making a solid water-soluble glyphosate salt-containing composition are known. For example, in U.S. Patent No. 5,047,079 which issued on September 10, 1991 to Djafar, there is disclosed a

5 method for preparing a phytotoxic composition comprising admixing highly hygroscopic isopropylamine salt of glyphosate acid with a molten surfactant to form a matrix, the surfactant being a solid at ambient temperatures.

10 In U.S. Patent No. 5,070,197 which issued on December 3, 1991 to Chin, et. al. an extrusion method is disclosed in which a Bronsted acid, N- phosphonomethylglycine for example, is intimately admixed with sodium hydroxide in an extruder to produce

15 a granular extrudate having a residual moisture content of no greater than 10%. Another method involving the production of a dry sodium glyphosate composition, albeit not involving extrusion, is disclosed in PCT application Publication No. WO 87/04595.

20 In U.S. Patent No. 5,266,553 which issued on November 30, 1993 to Champion, et. al. there is disclosed a method for preparing a dry, water-soluble salt of bentazon or of a herbicide containing a carboxylic acid functionality which involves repeated

25 treatments of the salt with a neutralizing base selected from the group consisting of ammonia, an alkylamine, a hydroxyalkylamine, an alkaline salt of an alkali metal and combinations thereof.

In French Patent Publication No. 2.692.439 which

30 was filed on May 19, 1993 and is assigned to Productos Osa SACIFIA, there is generally described a phytotoxic preparation comprising the monoammonium salt of N- phosphonomethylglycine as a powder or granule in combination with a wetting agent, surfactant and/or a

35 pulverulent additive. As exemplified in the reference,

the monoammonium salt is derived from reacting glyphosate acid with ammonium bicarbonate.

U.S. Patent No. 5,324,708 which issued on June 28, 1994 to Moreno, et. al. discloses a composition and 5 related methods for preparing and using a non-hygroscopic monoammonium glyphosate salt such as the mono-isopropylammonium salt of N-(phosphono-methyl)-glycine and the mono-isopropylammonium salt of (3-amino-3-carboxypropyl)-methane phosphonic acid in dry powder 10 form [sic].

In PCT application Publication No. WO 94/10844, published on May 26, 1994, a dry glyphosate composition is disclosed in which N-phosphono-methylglycine is admixed with, inter alia, an inorganic or organic, non- 15 caustic base material such as diammonium phosphate or a basic guanidine salt such as guanidinium acetate.

EPO application Publication No. 0 394 211 which was published on October 24, 1990, discloses an invention comprising a dry pesticidal composition and related 20 methods for use and production. More particularly, the invention relates to the enhanced solubility of the pesticidal composition as achieved by the addition of an effective amount of an organosilicone block copolymer or a fluorocarbon wetting agent.

25 In PCT application Publication No. WO 90/07275 which was published on July 12, 1990, there is disclosed an invention by which granular, water-soluble glyphosate compositions are made as by admixing, pan granulation, drying, spraying and extrusion.

30 In PCT application Publication No. WO 92/12637, which was published on August 6, 1992, there is disclosed an invention relating to a dry, water soluble glyphosate including a composition comprising substantially nonreacted glyphosate, an acid acceptor 35 such as sodium acetate and a liquid or solid surfactant.

All of the foregoing patents and publications are herein incorporated by reference.

The related art, as described, indicates that considerable effort has been directed toward formulating 5 compositions and related methods for making and using dry glyphosates. However, none of the above-identified references discloses a practical method for producing a dry, water-dispersible, water-soluble and appreciably non-hygroscopic ammonium glyphosate composition which is 10 capable of absorbing/adsorbing an exceptionally high level of adjuvants from N-phosphonomethylglycine and relatively inexpensive aqueous ammonium hydroxide on a manufacturing scale at an acceptable cost.

Thus, a need unsatisfied by known technology exists 15 within the art for the present invention which accomplishes these and other objectives.

20

Summary Of The Invention

The unresolved needs of the art are satisfied by the present invention which provides a highly desirable ammonium glyphosate dry plant growth regulator/herbicide 25 composition and novel method for producing the composition whereby the disadvantages associated with known dry compositions and related methods, as discussed, are overcome through heretofore unknown and undisclosed limitations.

30 In accordance with the present invention glyphosate acid is charged to, as for example, a suitable blender such as a ribbon blender where it is blended and then, if necessary, partially pre-dried by recirculation through a hot air grinding/drying system.

35 While the acid is being continuously recirculated, a solution of cooled ammonium hydroxide is added, as by

spraying, at a particular and critical rate to react with the acid. After a specified amount of ammonium hydroxide has been added, the reaction mass/product of the reaction, which is in the form of a powder, is

5 suitable for end use as a herbicide or as a plant growth regulator.

In addition, and perhaps more importantly, the powdered reaction product due to its highly sorptive character is capable of being further formulated to

10 absorb/adsorb an exceptionally high level of an adjuvant such as a wetting agent, an anti-foaming agent and particularly a surfactant composition. Thus, when so formulated, a very useful and highly desirable adjuvant-loaded product is formed which is every bit as good and

15 effective as comparable products obtained by prior art processes which require more expensive starting materials.

Optionally, the powdered reaction product or the adjuvant-loaded product may be granulated to provide a

20 free-flowing (i.e. non-caking), substantially dust-free and water soluble ammonium glyphosate herbicide and/or plant growth regulator.

Still further optional procedures may be carried out using the powdered reaction product. For example,

25 the powder may be further ground and/or dried prefatory to packaging. Significant advantages achieved by the present invention reside in its relative simplicity, comparative low cost and in the fact that no highly specialized equipment is required to practice the

30 invention. Thus, where conventional blending and milling/grinding equipment already exist, the present invention can be carried out efficiently on a commercial scale to produce a very high quality dry ammonium glyphosate product.

Figure 1 is a schematic diagram illustrating the process for preparing dry ammonium glyphosate in accordance with the present invention.

5 Detailed Description of the Preferred Embodiment

The present invention relates to a novel method for reacting N-phosphonomethylglycine (glyphosate acid) with ammonium hydroxide to produce ammonium glyphosate powder, a key raw material which may be used as is or in 10 granulated form or as a starting material in the formulation of a granulated surfactant-loaded dry glyphosate composition.

Until now, a comparatively inexpensive, effective and practical method for producing dry ammonium 15 glyphosate powder which is capable of being further formulated to absorb/adsorb an exceptionally high level of an adjuvant using aqueous ammonium hydroxide has not been known.

Instead, various alternate and less advantageous 20 methods have been developed by which ammonium glyphosate as well as alkali metal glyphosates such as sodium glyphosate have been made in dry, powder form. For example, sodium glyphosate has been produced by reacting glyphosate acid with sodium acetate or by extruding the 25 acid with sodium hydroxide as described above in PCT application Publication No. WO 92/12637 and U.S. Patent No. 5,070,197 respectively.

Sodium glyphosate granules and powders have, until 30 now, provided satisfactory dry glyphosate compositions. However, when compared to ammonium glyphosate salt compositions, the sodium salt is much more hygroscopic meaning it is not as resistant against ambient humidity. Thus, the sodium glyphosate salt is considered more difficult and more expensive to process as a dry 35 composition and, once formed as such, it has a greater

tendency to agglomerate which results in undesirable "caking" of the finished material.

Also, due to the relative molecular weights of ammonia and sodium, sodium glyphosate salt compositions 5 have a lower concentration of the active glyphosate than their counterpart ammonium glyphosate salt compositions. In addition, the per pound cost of sodium cation is much more expensive than the cost of obtaining the ammonium cation. The comparative disadvantages of sodium 10 glyphosate compositions are, thus, apparent.

As previously noted, certain solid/solid reaction methods are known for making dry ammonium glyphosate. Reacting ammonium bicarbonate with glyphosate acid, for example, as described above in French Publication No. 15 2,692,439 is believed to yield a dry ammonium glyphosate composition.

The invention disclosed herein, however, constitutes an advance in the art of making dry ammonium 20 glyphosate even over known methods utilizing ammonium bicarbonate.

For example, in practicing the present invention which involves reacting liquid ammonium hydroxide with solid N-phos-phonomethylglycine, it has been observed that the per pound cost of obtaining ammonium cation 25 derived from ammonium bicarbonate is approximately ten to twenty times more expensive than the per pound cost of obtaining an equivalent amount of the same cation from ammonium hydroxide. In the large-scale commercial production of ammonium glyphosate, this cost 30 differential alone strongly militates in favor of an effective method, such as that disclosed herein, for producing a solid ammonium glyphosate using ammonium hydroxide as the source of ammonium cation.

As used herein the terms "solid" and/or "dry" mean 35 the physical state in which the formulation has a specific shape and volume and resists deformation. The

solid may take the form of pellets, flakes, granules, powder or the like. Further, it will be understood that the solid formulation may subsequently be dissolved in a suitable diluent, usually and preferably water, and

5 applied to the locus where plant regulation or eradication is desired as by spraying or other conventional means.

From a technical perspective, the simple admixture of N-phosphonomethylglycine in commercially standard

10 "wet cake" form (i.e. having a moisture content of approximately 6-20 wt.%) with liquid ammonium hydroxide in stoichiometric quantities yields a viscous, "dough-like" product that is not compatible with conventional equipment for further processing. Such a product has a

15 physical character wholly distinct from the product generated by the process of the present invention. Thus, adherence to the process of the present invention and the manner and extent to which the reaction between the glyphosate acid and the ammonium hydroxide is

20 controlled in accordance with the process, are critical in ensuring the creation of a solid, free-flowing (i.e. non-caking) and water soluble ammonium glyphosate salt which, importantly, is capable of being further formulated to absorb/adsorb an exceptionally high level

25 of adjuvants such as surfactants.

In accordance with the process of the present invention, the reactant mixture is continuously dried and conditioned to maintain a suitable moisture content throughout the step of ammonium hydroxide addition such

30 that a free-flowing, readily handleable, powder is generated. This not only allows processing in conventional equipment, but also produces an ammonium glyphosate powder that can be used to make dry glyphosate products highly-loaded with adjuvants.

35 The inventors have determined that the moisture content in the reaction mass during the ammonium

hydroxide addition to the glyphosate acid is a critical aspect of the invention.

The amount of ammonium hydroxide which is required in order to practice the invention is equivalent to that 5 amount which is required to achieve approximately 95-105% neutralization of the acid which can be determined by conventional analytical methods known to those ordinarily skilled in the art such as by pH measurement.

In accordance with the process of the present 10 invention, the wet cake is charged to an actuated and suitable conventional blender. A pre-determined quantity of sodium sulfite may be added to prevent the possible formation of nitrosamines. Although the addition of sodium sulfite is not necessary to practice 15 the invention and does not affect the reaction between the glyphosate acid and ammonium hydroxide, certain governmental regulations require that nitrosamine levels in products of this nature be below 1 ppm. Experience has shown that, when added, the effective range of 20 sodium sulfite to be added as ensurance against the presence of unacceptable levels of nitrosamines is between 0.2 and 1.0 wt.% of the dried, finished product.

A pre-drying step, if required, occurs next during 25 which the wet cake and, if desired, sodium sulfite are continuously circulated through a hot air drying and milling system which is arranged in communication with the blender. A constant and elevated drying air temperature of about 170 to 300 degrees Fahrenheit, and 30 preferably 250° to 270° F, is maintained and the mixture is continuously circulated until its total moisture content is below about 6 wt.%. To determine the existence of this condition, a sample of the mixture is then recovered and assayed. If the moisture content of 35 the wet cake starting material is already below about 6 wt.%, then the pre-drying step is unnecessary.

Next, the temperature of the drying air system is substantially reduced to a temperature of about 150 to 200 degrees Fahrenheit as the mixture continues to circulate.

A cooled solution of ammonium

- 5 hydroxide is then added to the mixture, as by spray application into the blender, to form an ammonium glyphosate reaction mass. A standard commercial ammonium hydroxide solution is employed; preferably one that contains approximately 29 wt.% ammonia. The
- 10 solution is first cooled to about 40 to 50 degrees Fahrenheit because it is known that liquid ammonium hydroxide is volatile and that it boils at 86 degrees Fahrenheit. Thus, ammonium hydroxide loss is controlled and the likelihood of atmospheric pollution by the
- 15 evaporating solution is reduced.

The manner and rate at which the ammonium hydroxide is introduced are very significant. Preferably, the solution is sprayed, as by one or more nozzles into the blender containing the wet cake and sodium sulfite, if present, using a coarse spray. The flow of the sprayed solution is metered such that the moisture content of the reaction mass consistently decreases from the initial concentration of circa 6 wt.% down to about 2 wt.% (i.e. loss of weight on drying or LOD) or less during the period in which the ammonium hydroxide is added and the exothermic reaction proceeds.

Under the process conditions specified, the ammonium hydroxide spray rate is designed in such a way as to control the rate at which water is introduced with the ammonium hydroxide and formed as a product of the reaction between the glyphosate acid and the ammonium hydroxide. The object is to introduce the water at a rate slower than the rate at which moisture is being driven from the wet cake/sodium sulfite mixture due to the circulating dryer system.

Other ammonium hydroxide addition rates were experimented with but did not yield the highly desirable product generated by the present invention. For example, when the ammonium hydroxide was introduced

5 under the same process conditions but at a 40% higher rate, the ammonium glyphosate powder produced had less sorptive capacity rendering it unfit for further processing such as loading with adjuvants and particularly with surfactants. Addition rates in

10 excess of the 40% higher rate have an immediate adverse effect on the physical characteristics of the reaction mass; the reaction mass becomes a very wet and "dough-like" cohesive mass rendering it unsuitable for completion of the process.

15 Also, for example, if the glyphosate acid and sodium sulfite mixture is not pre-dried to below about 6 wt.%, the material in the blender again also becomes very wet and "dough-like" rendering it unsuitable for use in completing the process.

20 It is appreciated that the pre-drying step may be avoided or abbreviated such that the moisture content in the mixture of glyphosate acid and sodium sulfite may be initially greater than about 6 wt.%. However, it is also known that the ammonium hydroxide addition rate

25 under such circumstances would be so slow as to render the process economically unfeasible.

As the process proceeds, samples should periodically be obtained and assayed to measure the moisture content to ensure that the rate of water

30 removal from the reaction is greater than the rate at which water is being added. This can simply be determined by observing progressive decreases in the moisture content of the mixture.

The above-described process conditions should be

35 maintained until all of the ammonium hydroxide has been added. At this point, the ammonium glyphosate is in the

form of a powdered product which may be further processed. Such further processing may include: the addition of sodium sulfite, grinding, drying, granulating or formulating with adjuvants.

5 The decision regarding which, if any, of these further processes is to be performed is dictated, largely, based upon the intended end-use of the product.

Regardless of the further processing selection,

10 however, a quantity of sodium sulfite may be again optionally added. In conjunction with this step, the reaction mass may be further ground to make it more suitable for further processing. If further processing such as granulation or formulation with adjuvants is to

15 be performed immediately, it is not necessary to further dry the product at this stage. However, if the product is to be shipped or stored for more than a few days, for example, then it should be further dried to less than 1 wt.% moisture at this time to prevent caking.

20 Where it is desired to use the product without the addition of any adjuvants as a herbicide or plant growth regulator, then it is desirable to granulate or agglomerate it, such as by pan granulation and drying or by other methods known in the art.

25 Should it be desirable to produce a product containing adjuvants such as surfactants, anti-foaming agents, wetting agents and the like, these may be added as by blending in suitable equipment and, preferably, by kneading, extruding and drying or as by other methods

30 well-known to the ordinarily skilled artisan.

The following example illustrates production of the composition of the invention in accordance with the process described herein. All percentages are based upon weight, unless otherwise clearly indicated.

In a plant-scale reactor system comprised of a stainless steel ribbon blender, a suitable hot air drying system such as an air-swept hammer mill supplied with hot air and an adapted dust collector, all of which

5 were in communication with each other as by suitable connecting conduits, 2400 lbs. of standard grade N-phosphonomethylglycine "wet cake" having an assayed moisture content of about 10% LOD was charged to the ribbon blender where it was immediately mixed.

10 Once all of the wet cake had been deposited in the ribbon blender, 4.8 lbs. of solid sodium sulfite was also charged to the blender and combined with the wet cake whereupon it was intimately mixed. The combination of wet cake and sodium sulfite was then circulated

15 within the hot air-swept mill system using an air inlet temperature of about 250° F for one hour. A sample of the mixture was then recovered and assayed to determine its moisture content/LOD.

When the moisture content of the mixture was

20 reduced to approximately 6%, the material continued to be circulated through the drying system and the air inlet temperature to the mill was reduced to about 170° F.

With the air temperature within the system being

25 maintained at about 170° F, a solution of ammonium hydroxide (29% NH₃), previously cooled to a temperature of between 40 to 50° F, was then pumped to the ribbon blender and coarsely sprayed by five adjustable nozzles onto the glyphosate acid to form a reaction mass. A

30 total quantity of 730 lbs. of liquid ammonium hydroxide was introduced by spraying. A rate not exceeding 3.5 lbs./minute was established for feeding the liquid ammonium hydroxide.

During the approximately 3.5 hours that were

35 required to feed all of the ammonium hydroxide solution, several samples of the circulating mixture were obtained

and assayed to ensure that the rate of ammonium hydroxide addition provided for the progressive reduction of the total moisture content of the reaction mass. At the conclusion of the ammonium hydroxide 5 addition, the reaction mass was a free-flowing powdered product particularly well-suited for immediate and desirable further processing.

In the process which gave rise to this Example 1, it was intended that the reaction mass be further 10 processed at a later time. In view of this fact, the reaction mass was, at this point, conditioned in such a way as to ensure that it would not cake during storage. First, however, an additional and equal quantity of sodium sulfite was charged to the blender and mixed for 15 approximately ten minutes to ensure uniform dispersion with the powdered reaction mass.

This combination was next physically comminuted by passing the dry powdered composition through an air classifying mill to reduce the discrete particles of the 20 composition to a substantially small and uniform size. Although the air classifying mill was used because it happened to be a part of the equipment train used for this Example 1, this milling procedure is not required to practice the invention.

25 Following comminution, the product was subjected to conventional fluid bed drying to ensure that the resulting finished product exhibited a residual moisture content of no greater than 1.0% LOD.

From the starting materials which included 2400 30 lbs. of glyphosate acid (i.e. "wet cake" containing about 10% moisture), a total of 9.6 lbs. of sodium sulfite (optionally) and 730 lbs. of liquid ammonium hydroxide, a theoretical product yield of 2394 lbs. of dry, powdered ammonium hydroxide having a residual 35 moisture content of approximately 0.5% can be obtained.

In addition to possessing highly desirable commercial product qualities, the product obtained in connection with the foregoing example has demonstrated excellent storage and stability characteristics. In fact when stored properly, as for example in sealed polyethylene bags, the product has proven not to degrade or cake after more than six months of actual warehousing.

10 As discussed in some detail above, the powdered reaction mass/product produced in accordance with the novel process of this invention is particularly well adapted to be further formulated to absorb/adsorb high levels of adjuvants.

15 In combination, the relative simplicity of the present invention, its ability to be practiced using conventional equipment and the comparative low cost of the ammonium cation furnished by ammonium hydroxide deem very significant the capacity of the powdered reaction mass/product to absorb/adsorb high levels of adjuvants.

20

While the choice of a particular adjuvant or combination of adjuvants will be easily made by those ordinarily skilled in the art without undue experimentation, Example 2 presented below illustrates the exceptional sorptive capacity of the powdered reaction mass/product when loaded with surfactant.

30

EXAMPLE 2

The powdered reaction mass/product formed by the process described in Example 1 can be used to make a dry formulation of ammonium glyphosate containing a high level of surfactant of at least about 20 wt.%.
35

To make such a highly loaded product, 16 kilograms of the powdered reaction mass/product is blended with 4 kilograms of a polyoxyethylene alkylamine surfactant and 1.4 kilograms of water in a jacketed batch kneader, such

5 as a Fuji Paudal, for approximately 10 minutes with water at a temperature of about 80° C circulating in the jacket. The dough that is formed is then extruded, as for example in a Fuji Paudal twin screw extruder, fitted with screens having approximately 1 mm. diameter

10 borings. The extrudate obtained consisted of discrete, "spaghetti-like" short noodles which did not stick together and which were easily and conveniently dried, such as for example in a Fitz-Aire fluid bed dryer, without formation of undesirable lumping.

15 To illustrate the significance of the process of the present invention as it pertains to the sorptive character of the powdered reaction mass/product, a product made in accordance with all of the process variables of the invention but, wherein the addition

20 rate of ammonium hydroxide solution was 40% higher, a doughy product was produced that was undesirably wet and sticky to touch. Further, the extrudate produced therefrom consisted of undesirably long "spaghetti-like" noodles that stuck together and formed large

25 agglomerates. This extrudate was very difficult to fluidize in the fluid bed dryer and resulted in the formation of a large quantity of dried agglomerates which, in order to be usable, would then have to be ground and recycled back through the extrusion process.

CLAIMS

What We Claim Is:

5 1. A method for preparing a dry ammonium N-phosphono-methylglycine phytoactive composition capable of being highly loaded with one or more adjuvants which comprises reacting aqueous ammonium hydroxide with N-phosphonomethylglycine in a conventional reactor system

10 to form a reaction mass such that the moisture content of said reaction mass is continuously decreased throughout the reaction.

15 2. The method of Claim 1 further comprising the step of drying said N-phosphonomethylglycine prior to reacting it with said ammonium hydroxide.

20 3. The method of Claim 1 wherein said ammonium hydroxide and said N-phosphonomethylglycine are reacted in approximately equivalent molar amounts.

25 4. The method of Claim 1 wherein the reaction is carried out in conventional blending equipment such as in a ribbon blender.

30 5. The method of Claim 1 wherein the moisture content of said reaction mass is continuously decreased throughout the reaction by circulating said reaction mass through an air swept mill or equivalent using air heated to a temperature of about 150° F to about 300° F.

35 6. The method of Claim 2, wherein said drying is accomplished by circulating said N-phosphonomethylglycine through an air swept mill system or equivalent using air heated to a temperature of about 230° F to about 280° F.

7. The method of Claim 1 wherein said ammonium hydroxide is any commercially available aqua ammonia solution.

8. The method of Claim 1 wherein the moisture content of said N-phosphonomethylglycine is within the range of about 7 wt.% to about 20 wt.%.

9. The method of Claim 5 wherein the air is heated to a temperature within the range of about 150° F to about 200° F.

10. The method of Claim 1 wherein said moisture content of said reaction mass is less than approximately 2 wt.% at the conclusion of said reaction.

15 11. The method of Claim 2 wherein the molar ratio of ammonia to N-phosphonomethylglycine in said reaction mass is approximately 0.95:1.0 to 1.05:1.0.

12. The method of Claim 2 wherein said reactor 20 system comprises at least a conventional blender and hot air dryer and wherein said N-phosphonomethylglycine is dried by circulation through said reactor system which is heated to about 250° F to about 280° F until its moisture content is reduced to about 6 wt.% or below.

25

13. The method of Claim 2 wherein said ammonium hydroxide solution is an aqueous solution containing approximately 29 wt.% ammonia cation.

30 14. A method for preparing a phytoactive ammonium glyphosate comprising:

(a) charging to a suitable reactor system a first molar quantity of glyphosate acid wet cake having a moisture content of up to about 20 wt.%;

35 (b) introducing a second molar quantity, equivalent to said first molar quantity, of ammonium

hydroxide to said reactor system containing said glyphosate acid; and

(c) controlling the reaction that occurs between said glyphosate acid and said ammonium hydroxide such 5 that the moisture content in the reaction mass/product thereby produced consistently decreases.

15. The method of Claim 14 further including the step of pre-drying said glyphosate acid to reduce its 10 moisture content to about 5 wt.% to about 8 wt.% prior to the introduction of said ammonium hydroxide.

16. The method of Claim 15 wherein said pre-drying is accomplished by circulating said glyphosate acid 15 through a hot air dryer which is a part of said reactor system.

17. The method of Claim 16 wherein the air temperature within said hot air dryer is about 200° F to 20 about 300° F during said pre-drying.

18. The method of Claim 17 wherein said glyphosate acid continues circulating through the hot air dryer of said reactor system during the step in which said 25 ammonium hydroxide is introduced and wherein, prior to the introduction of said ammonium hydroxide, the temperature within said hot air dryer is reduced to a temperature of about 150° F to about 180° F and maintained until the introduction of said ammonium 30 hydroxide is complete.

19. The method of Claim 18 wherein said ammonium hydroxide is first cooled to a temperature of between about 40° F to about 50° F and then introduced to said 35 reactor system and reacted with said glyphosate acid in the form of a coarse spray.

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20. The method of Claim 19 wherein said reaction mass/product is a highly sorptive, free-flowing powder having a moisture content of about 2 wt.% or less.

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**LIQUID/SOLID PROCESS USING AMMONIUM HYDROXIDE
TO MAKE AMMONIUM GLYPHOSATE**

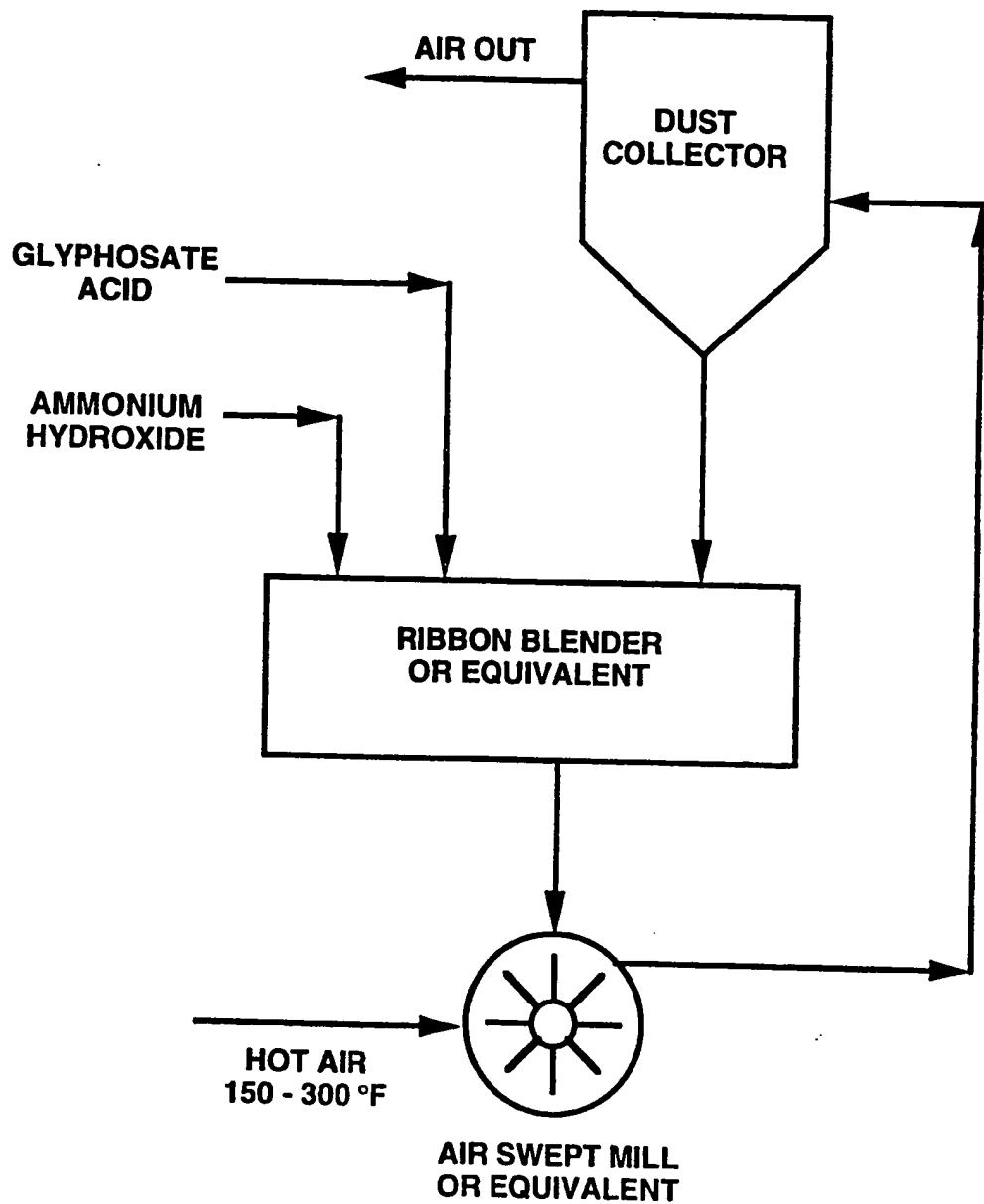


FIG. 1

INTERNATIONAL SEARCH REPORT

Int'l Application No
PCT/US 96/03081

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C07F9/38

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C07F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 256 608 (STAUFFER CHEMICAL CO) 24 February 1988 cited in the application see the whole document ---	1-20
A	EP,A,0 238 240 (UNIROYAL CHEM CO INC) 23 September 1987 cited in the application see the whole document ---	1-20
A	US,A,5 266 553 (CHAMPION JAMES K ET AL) 30 November 1993 cited in the application see the whole document ---	1-20
		-/-

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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*'Z' document member of the same patent family

Date of the actual completion of the international search

16 July 1996

Date of mailing of the international search report

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Beslier, L

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 96/03081

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	FR,A,2 692 439 (OSA SACIFIA PROD) 24 December 1993 cited in the application see the whole document ---	1-20
A	WO,A,92 18513 (ALKALOIDA VEGYESZETI GYAR) 29 October 1992 cited in the application see the whole document ---	1-20
A	EP,A,0 582 561 (MONSANTO CO) 9 February 1994 see the whole document ---	1-20
A	WO,A,90 07275 (MONSANTO CO) 12 July 1990 cited in the application see the whole document -----	1-20

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 96/03081

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A-0256608	24-02-88	CA-A-	1309266	27-10-92
		DE-A-	3778089	14-05-92
		DK-B-	170456	11-09-95
		JP-B-	8025849	13-03-96
		JP-A-	63051307	04-03-88
		RU-C-	2038790	09-07-95
		US-A-	5047079	10-09-91
EP-A-0238240	23-09-87	AU-B-	602137	04-10-90
		AU-B-	7019587	24-09-87
		CA-A-	1297696	24-03-92
		DE-D-	3787107	30-09-93
		DE-T-	3787107	20-01-94
		ES-T-	2058106	01-11-94
		JP-C-	1714157	27-11-92
		JP-B-	4001721	14-01-92
		JP-A-	62230701	09-10-87
		US-A-	5070197	03-12-91
		ZA-A-	8701571	24-08-87
US-A-5266553	30-11-93	NONE		
FR-A-2692439	24-12-93	BR-A-	9300433	08-09-93
WO-A-9218513	29-10-92	HU-A-	72428	29-04-96
		HU-A-	72429	29-04-96
		HU-A-	72427	29-04-96
		AT-T-	139236	15-06-96
		AU-B-	653226	22-09-94
		AU-B-	1653592	17-11-92
		BG-A-	97162	30-06-94
		BR-A-	9205234	27-07-93
		CA-A-	2084663	17-10-92
		EP-A-	0537318	21-04-93
		JP-T-	6500339	13-01-94
		PL-A-	297358	10-01-94
		SK-A-	366992	10-05-95
		US-A-	5410075	25-04-95
		US-A-	5324708	28-06-94
		LT-A,B	129	25-09-94

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 96/03081

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A-0582561	09-02-94	AU-B-	4432493	03-02-94
		CA-A-	2101669	01-02-94
		JP-A-	6256121	13-09-94
		NZ-A-	248289	24-02-95
-----	-----	-----	-----	-----
WO-A-9007275	12-07-90	AT-T-	139670	15-07-96
		AU-B-	635514	25-03-93
		AU-B-	4833390	01-08-90
		CA-A-	2006816	30-06-90
		EP-A-	0378985	25-07-90
		EP-A-	0452366	23-10-91
		JP-T-	4502618	14-05-92
-----	-----	-----	-----	-----